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The First Examples of Improved Catalytic Asymmetric C-C Bond Formation Using the Monodentate Ligand Combination Approach

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Supporting Information

General. All reactions were carried out under nitrogen atmosphere using dried glassware. All reagents and substrates were obtained from commercial sources were used without purification unless stated otherwise. Dioxane was distilled from sodium. THF was distilled from sodium/benzophenone. Arylboroxines were prepared from their parent arylboronic acids according to literature procedure.[1] Phosphoramidites **L2** and **L3** were prepared according to literature procedure.[2] Chromatography: Merck silica gel Type 9385 230-400 mesh, TLC: Merck silica gel 60 F_{254}. ^{1}H- ,^{13}C- and ^{31}P-NMR spectra were recorded on a Varian Gemini 200 (200, 50.3 and 80.9 MHz, respectively) using $CDCl_3$ as solvent. Chemical shifts are reported in ppm with the $CHCl_3$ resonance as the internal standard for ^{1}H (δ 7.25), $CDCl_3$ for ^{13}C (δ 77.0), and external 85% H_3PO_4 for ^{31}P-NMR (δ 0.0). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a Perkin Elmer 241 polarimeter at room temperature. Mass spectra were recorded on a AEI-MS-902 mass spectrometer. GC measurements were performed on a HP 6890 gas chromatograph using a flame ionisation detector. HPLC analysis was carried out on a Water 600E system controller with a Water 991 photodiode array detector.

General procedure for the rhodium catalyzed boronic acid additions. In a Schlenk tube 2.58 mg (10 μmol, 2 mol%) of $Rh(acac)(C_2H_4)_2$ and two 12.5 μmol (2.5 mol%) portions of phosphoramidite were dissolved in 1 mL of anhydrous dioxane and stirred at room temperature for 15 min. 0.5 mmol of the Michael acceptor, 10 μL of tridecane (internal standard for GC) and 0.67 mmol of arylboroxine were added sequentially and the resulting mixture was stirred for 2 min. After the addition of 36 μL (2.0 mmol) of water the mixture was degassed and stirred for 3 hours at 60 ^{o}C. The reaction mixture was cooled to room temperature, quenched with sat. aq. $NaHCO_3$ and extraced with diethyl ether. The crude mixture was filtered over a patch of Na_2SO_4 and subjected to chiral GC or HPLC analysis.

1-Benzo[1,3,2]dioxaphosphol-2-yl-2,5-(R,R)-diphenyl-pyrrolidine (L1). To a solution of 1.74 g (10 mmol) of 1,2 phenylene phosphorochloridite in 10 mL of anhydrous THF at 0 ^{o}C was added a solution of 2.23 g (10 mmol) 2,5-(R,R)-diphenyl-pyrrolidine[3] and 1.01 g (10 mmol) triethylamine in 5 mL of anhydrous THF. The resulting white turbid mixture was stirred at 0 ^{o}C for 1 hour. The solvent was removed under reduced pressure and the product was purified with column chromatography (pentanes/diethyl ether 10/1, R_f 0.9) to give 2.16 g (6 mmol, 60% yield) of **L1** as a white solid. ^{1}H-NMR δ: 7.13 (m, 10H), 6.98 (d, *J*= 7.6 Hz, 1H), 6.75 (dt, *J*= 7.6, 1.4 Hz, 1H), 6.54 (dt, *J*= 7.6, 1.1 Hz, 1H), 5.97 (d, *J*= 7.6 Hz, 1H), 4.90 (d, *J*= 5.1 Hz, 2H), 2.33 (m, 2H), 1.66 (m, 2H) ppm. ^{13}C-NMR δ: 145.0 (s), 128.1 (d), 126.7 (d), 126.1 (d), 121.5 (d), 121.2 (d), 111.4 (d), 110.3 (d), 63.2 (d), 63.0 (d), 33.6 (t) ppm. ^{31}P-NMR δ: 143.8 ppm. HRMS calcd for $C_{22}H_{20}NO_2P$ 361.1231 found 361.1222. Anal. calcd for $C_{22}H_{20}NO_2P$ C 73.12; H 5.58; N 3.88 found C 73.09; H 5.58; N 3.89. $[\alpha]_D$ –104^{o} (*c* 1.15, $CHCl_3$)

2-Phenyl-2-(4-methylphenyl)-nitroethane (2). Spectral data were in accordance with literature.[4] Enantiomer separation with chiral HPLC, DAICEL OJ, heptanes/2-propanol 9/1, 210 nm, rt 13.4, 17.3 min.

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4-Phenyl-4-p-tolyl-butan-2-one (4). Spectral data were in accordance with literature.[5] Enantiomer separation with chiral HPLC, DAICEL OD, heptanes/2-propanol 99/1, 210 nm, rt 12.7, 14.3 min.

3-Phenylcyclohexanone (6). Spectral data were in accordance with literature.[6] Enantiomer separation with chiral GC, Astec α-TA, 120 °C, rt 58.0, 60.1 min.

NMR of the R(Lx)(Ly) complexes. In a nitrogen filled NMR sample tube 3.22 mg (12.5 μmol, 1 eq) of $Rh(acac)(C_2H_4)_2$ and two 12.5 μmol (1 eq) portions of phosphoramidite were dissolved in 0.6 mL of $CDCl_3$. The spectra were aquired with a T_1 of 1.2 sec. and a 90° pulse. Rh(acac)(**L1**)$_2$ ^{31}P-NMR δ: 157.4 (d, J_{Rh-P}=282 Hz) ppm. Rh(acac)(**L2**)$_2$ ^{31}P-NMR δ: 159.4 (d, J_{Rh-P} =300 Hz) ppm. Rh(acac)(**L3**)$_2$ ^{31}P-NMR δ: 161.8 (d, J_{Rh-P} =299 Hz) ppm. Rh(acac)(**L1**)(**L2**) ^{31}P-NMR δ: 162.4 (d, J_{Rh-P} =294 Hz) minor, 161.2 (d, J_{Rh-P} =294 Hz) major, 160.7 (d, J_{Rh-P} =282 Hz) major, 159.5 (d, J_{Rh-P} =282 Hz) ppm minor.[7,8] Rh(acac)(**L1**)(**L3**) ^{31}P-NMR δ: 160.7 (d, J_{Rh-P} =289 Hz) minor, 159.5 (d, J_{Rh-P} =289 Hz) major, 158.7 (d, J_{Rh-P} =285 Hz) major, 157.5 (d, J_{Rh-P} =285 Hz) ppm minor.[7,8] Rh(acac)(**L2**)(**L3**) ^{31}P-NMR δ: 160.6 (d, J_{Rh-P} =301 Hz), 160.5 (d, J_{Rh-P} =301 Hz) ppm.[7]

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[7] Only a Rh-P coupling is observed, no P-P coupling is detected, for other such examples see Crumbliss, A.L.; Topping, R. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, Florida, 1987; Chapter 15.
[8] Two sets of two doublets are observed due to a parallel and an anti-parallel arrangement of the phosphoramidite ligands in the hetero-complex.